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THERMAL DECOMPOSITION AND EXPLOSION OF AMMONIUM PERCHLORATE AND AMMONIUM PERCHLORATE PROPELLANT UP TO 50 KILOBARS (5.0×10^9 N/m²)

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16. Abstract <p>The rates of thermal decomposition of ammonium perchlorate and an ammonium perchlorate solid propellant at 15, 25, and 50 kilobars (1.5×10^9, 2.5×10^9, and 5.0×10^9 N/m²) pressure were studied in a cubic anvil press. The data were correlated by first order rate equations to obtain the temperature variation of the specific reaction rates and the apparent activation energies. Explosion limits of pure ammonium perchlorate are included to 30 kilobars (3.0×10^9 N/m²). Electrical resistance measurements of this salt at high pressure were also made.</p>				13. Type of Report and Period Covered Technical Note	
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THERMAL DECOMPOSITION AND EXPLOSION OF AMMONIUM PERCHLORATE AND AMMONIUM PERCHLORATE PROPELLANT UP TO 50 KILOBARS (5.0×10^9 N/m²)

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SUMMARY

Thermal decomposition of ammonium perchlorate (AP) and an AP based propellant was studied at high pressure in a cubic anvil press. Preexplosion kinetics of the thermal decomposition of AP and propellant were determined between 266° and 337° C at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and 5.0×10^9 N/m²). First-order kinetics were observed in all cases. Arrhenius plots of reaction-rate constants at different decomposition temperatures allowed the calculation of activation energies. For AP the energies ranged from 40.4 kilocalories per mole (1.69×10^5 J/mole) at 15 kilobars (1.5×10^9 N/m²) to 57.2 kilocalories per mole (2.39×10^5 J/mole) at 50 kilobars (5.0×10^9 N/m²). Activation energies for propellant were calculated to be 30.3 kilocalories per mole (1.27×10^5 J/mole) at 15 kilobars (1.5×10^9 N/m²) and 48.5 kilocalories per mole (2.03×10^5 J/mole) at 50 kilobars (5.0×10^9 N/m²).

Decompositions of AP were explosive at a heating rate of 10° C per minute. Explosion limit curves (T against P) showed explosion temperatures increasing with increasing pressure up to 30 kilobars (3.0×10^9 N/m²). Addition of small amounts of aluminum and copper chromite powders to AP and propellant reduced explosion temperatures from 10° to 60° C depending upon the pressure.

Electrical resistance of AP pellets at high pressure with temperature variation showed no discontinuities. This suggested that no phase transformations occurred.

INTRODUCTION

There is a great technological interest in ammonium perchlorate (AP) because of its extensive use in solid propellant rockets. In this work AP is subjected to pressures and temperatures where many materials undergo phase transformations. Perhaps the best known case of a phase transformation is the formation of diamond from graphite

(ref. 1). A phase change in AP would give a material with drastically different properties, which, in turn, might change the flame characteristics and burning rate.

The thermal decomposition of AP has been studied in great detail at atmospheric and reduced pressure. Studies of this material show several unique features. Bircumshaw and Newman (ref. 2) found that below 300°C the decomposition does not go to completion, but stops after about 30 percent of the salt has decomposed, leaving a residue with the same chemical composition. The kinetics and mechanism of decomposition are temperature dependent (ref. 3). Galwey and Jacobs (ref. 4) suggested that below 300°C an electron transfer mechanism involving radical formation is responsible for the decomposition. Galwey and Jacobs (ref. 5) also found that temperatures above 350°C cause the decomposition to go to completion. At these higher temperatures the reaction can be explained by either a proton transfer mechanism or rupture of chlorine-oxygen bonds. Above 440°C the decomposition is explosive (ref. 6). Deflagration characteristics of pure AP have been studied by means of a closed-bomb strand burning technique at pressures from 1000 to 23 000 psi (6.895×10^6 to 1.586×10^8 N/m^2) (ref. 7).

This investigation deals with the influence of pressure on the thermal decomposition of AP and an AP propellant in a multianvil high pressure apparatus. Preexplosion kinetics of AP and propellant are determined between 266° and 337°C at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and 5.0×10^9 N/m^2). Specific reaction-rate constants are calculated from first-order equations. These data permit calculation of the energy of activation for the decompositions. Explosion limits of AP are determined by heating compressed pellets of the salt at a slow, constant rate at fixed pressure. Data are given for the effect of finely divided aluminum powder and copper chromite additives on explosion limits. In addition, some data on the electrical resistance of AP at high pressure were obtained.

EXPERIMENTAL MATERIALS AND PROCEDURE

Materials

Ordinance grade AP (99.5 percent minimum purity), twice recrystallized from water, finely ground was used in this study. Bismuth, barium, and thallium, in wire form for calibration experiments, were high purity elements (>99.999 percent). Pyrophyllite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) is a naturally occurring substance and was used as received. The propellant used in this work contained 80 percent by weight polybutadiene-acrylic acid and 20 percent by weight AP. The AP was a mixture of 20 percent fine material ($11\text{-}\mu\text{m}$ average particle diameter) and 80 percent coarse ($88\text{-}\mu\text{m}$ average particle diameter).

Apparatus

All high pressure experiments performed in this study were carried out with a multianvil pressure apparatus of cubic configuration. The apparatus consists essentially of six hydraulically operated pistons to which are attached square-faced tungsten carbide anvils that form a cubic volume. Each piston is pushed inward along its axis against the material to be pressurized. The sample to be compressed is put into a pyrophyllite cube which is 10 to 15 percent larger in edge dimension than the 0.89-inch (2.26-cm) square anvil face. When the anvils touch the pyrophyllite cube, there are gaps between the anvils which allow forward movement of the anvils to compress the sample. As the anvils advance, some of the pyrophyllite extrudes into the gaps to form the gasket structure which gives support to the anvils and also absorbs some of the thrust load. Details of the apparatus have already been described (ref. 8).

Pressure Calibration

A pressure calibration of the apparatus must be determined before any pressure runs are made. Calibration is necessary because friction and pressure in the gasket areas absorb an unknown amount of the thrust force on the anvil faces. Therefore, the overall force-area ratio is not the true pressure in the center of the pressure chamber. The actual pressure calibration is accomplished by placing a material in the pressure chamber which is known to undergo an abrupt shift in electrical resistance or in volume at a definite pressure and determine the force at which the "known" transitions occur. The known transition pressures have been determined previously in a free-piston apparatus in which the pressure can be calculated accurately from the force-area ratio.

The pressure calibration of the apparatus in this work was determined by measuring the load required to convert BiI to BiII, BiII to BiIII, TlII to TlIII, BaII to BaIII, and BiV to BiVI. The bismuth, thallium, and barium were in wire form enclosed in cast silver chloride as shown in figure 1. The silver chloride acts as a nearly hydrostatic pressure transmitting medium. The accepted values of transition pressures for bismuth, thallium, and barium are those of Kennedy and La Mori (ref. 9). A typical transition curve of bismuth is given in figure 2 which shows sharp changes at the transition point when relative resistance is plotted against load. The electrical resistance of the calibration wire is followed by observing the potential drop across two opposed anvils at constant current. The resistance due to the anvils and copper leads is negligible. At the point where BiI \rightarrow BiII, the pressure required is $25\,410 \pm 95$ bars ($2.541 \times 10^9 \pm 9.5 \times 10^6$ N/m²). Figure 3 shows a calibration curve giving the transition values for bismuth, thallium, and barium plotted against press load. Load-resistance characteristics for

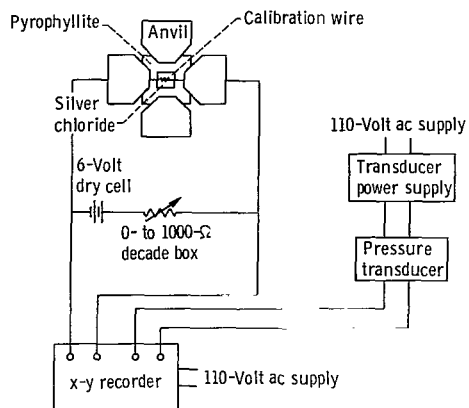


Figure 1. - Schematic diagram for pressure calibration.

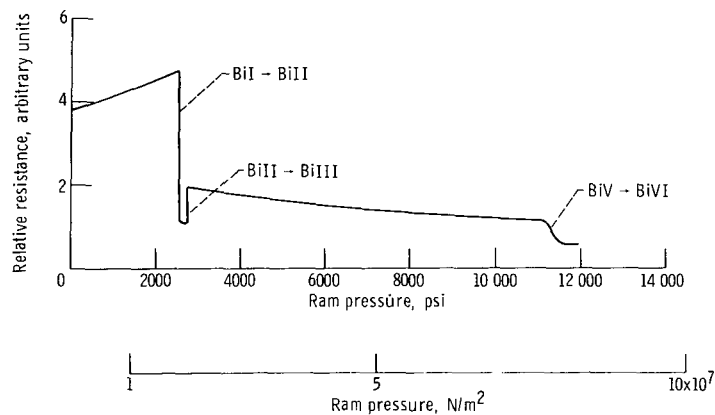


Figure 2. - Bismuth pressure transition curve.

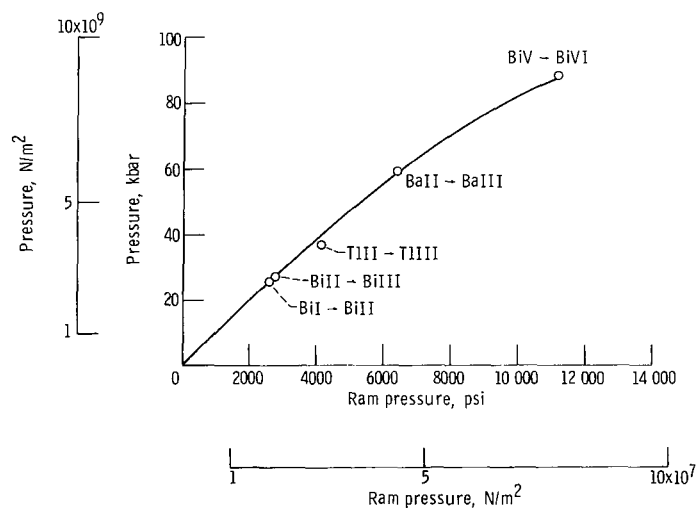


Figure 3. - Pressure calibration curve.

the calibration wires were observed on an X-Y recorder, the load signal being derived directly from a calibrated standard pressure cell and resistance from the potential drop across the wire at constant current.

Preexplosion Kinetics

AP samples for the kinetic study were prepared in the form of 3/8-inch- (0.95-cm-) diameter disks. They were made by compaction of 140 milligrams of polycrystalline powder in a pellet mold at 180 000 psi (1.241×10^9 N/m²) at room temperature. An AP pellet was then placed between tantalum foil backed up with stainless steel disks in a boron nitride container surrounded by a graphite cylinder as shown in figure 4. The

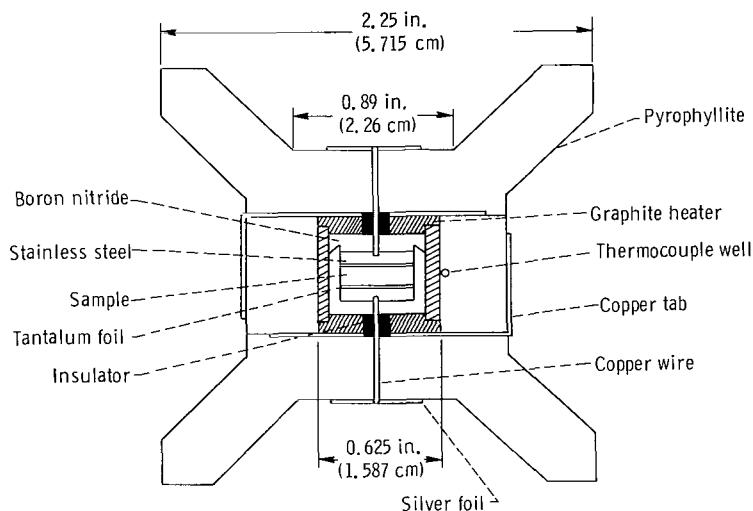


Figure 4. - Cross section of high pressure cell assembly.

graphite was resistively heated at the rate of 10⁰ C per minute by means of a welding transformer driven by a variable speed motor. Current was passed through two opposed anvils and led to the graphite heater by means of copper tabs. Massive pyrophyllite was used for specimen containers and as a solid pressure transmitting medium. Integral preformed gaskets were machined on the pyrophyllite cubes to minimize sample deformation during initial stages of pressure application (ref. 10). Sample temperatures as determined by thermocouple measurements at high pressure were kept constant within 0.5⁰ C. Sample temperatures were continuously monitored on an X-Y recorder.

The experiment was performed by compressing an AP pellet to the desired pressure,

raising the temperature to the desired level, and holding these conditions for a prescribed time. Then temperature and pressure were reduced to ambient conditions and the sample weighed to determine weight loss. The resulting weight loss records were analyzed to determine the dependence of decomposed AP upon time.

Explosion Limits

In these experiments the weight of AP was reproduced in different runs to 140 ± 1 milligrams. Samples were confined between 3-mil-thick tantalum foil. The AP pellets were brought to the desired pressure at room temperature and then heated at the rate of 10°C per minute. The temperature of explosion at the various pressures was determined by recording the temperature at which a detonation was clearly heard during the heating of the sample. As a result of the explosions, pyrophyllite was ejected from the gasket areas of the container with considerable force. Some explosions, particularly those at the higher pressures were of sufficient violence to damage or destroy the carbide anvils. For this reason explosion limits were determined only to 30 kilobars ($3.0 \times 10^9 \text{ N/m}^2$).

Electrical Resistance

Resistance measurements were made with an electrometer equipped with power supply and shunt. Contact with the AP pellet was made with tantalum foil backed up with stainless steel disks. The circuit to the exterior of the pyrophyllite cube was completed with copper wire and silver foil. Resistance was measured through two opposed anvils. The resistance of the electrical circuit excluding the AP pellet was negligible. Temperature was measured with Chromel/Alumel thermocouples placed near the perchlorate sample as shown in figure 4. The output of the electrometer and thermocouple were fed into X-Y recorders to plot the changes in resistance with temperature.

RESULTS AND DISCUSSION

Preexplosion Kinetics (Ammonium Perchlorate)

Rate data in the temperature range 282° to 337°C were obtained for the thermal decomposition of AP at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and $5.0 \times 10^9 \text{ N/m}^2$). A first-order reaction for the disappearance of the salt was assumed since plots of the logarithm of the mole fraction of remaining AP against time produced approximately

TABLE I. - DATA FOR PRESSURE RUNS (AMMONIUM PERCHLORATE)

Pressure, kbar (N/m^2)								
15 (1.5×10^9)			25 (2.5×10^9)			50 (5.0×10^9)		
Temperature, $^{\circ}\text{C}$	Time, min	Mole fraction remaining	Temperature, $^{\circ}\text{C}$	Time, min	Mole fraction remaining	Temperature, $^{\circ}\text{C}$	Time, min	Mole fraction remaining
282	6	0.920	293	5	0.925	312	5	0.923
	11	.865		10	.856		20	.728
	16	.802		25	.697		40	.544
	31	.652		40	.541		60	.397
	51	.520		60	.405		85	.278
	81	.370		80	.309			
295	1.5	0.958	305	5	0.858	324	4	0.835
	6.5	.815		10	.722		14	.548
	16.5	.615		20	.504		29	.306
	31.5	.443		35	.319		44	.158
	41.5	.353		60	.136		59	.085
	61.5	.212				337	5	0.554
305	1	0.922	312	1	0.943		10	.300
	6	.653		6	.726		15	.178
	16	.399		16	.425		20	.096
	26	.265		26	.243			
	46	.099		41	.113			
			324	4	0.597			
316	2.5	0.752		9	.319			
	7.5	.451		14	.182			
	12.5	.224		19	.091			
	17.5	.092						

straight lines. The data for these pressure runs are tabulated in table I. Figures 5 to 7 show the results obtained at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and 5.0×10^9 N/m^2). The decompositions in most cases were carried out to at least 80 percent completion. Values of the specific reaction-rate constants k were calculated from the slopes of the aforementioned plots and are shown in table II.

From reaction-rate theory (ref. 11), the rate constant k may be written as

$$k = Ae^{-E/RT}$$

where A is a constant independent of the nature of the reaction, E is the activation energy, R is the universal gas constant, and T is absolute temperature.

Figure 8 shows plots of log rate constants against $1/T$ for a number of runs at

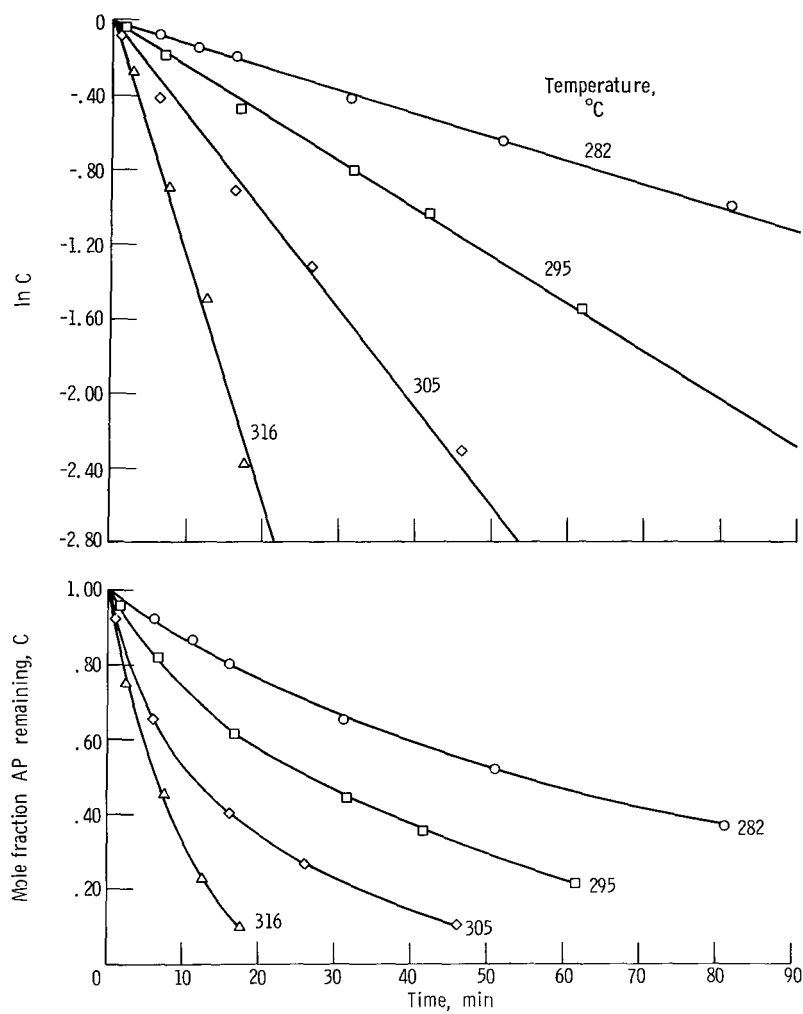


Figure 5. - Fraction of undecomposed ammonium perchlorate (AP) at 15 kilobars ($1.5 \times 10^9 \text{ N/m}^2$).

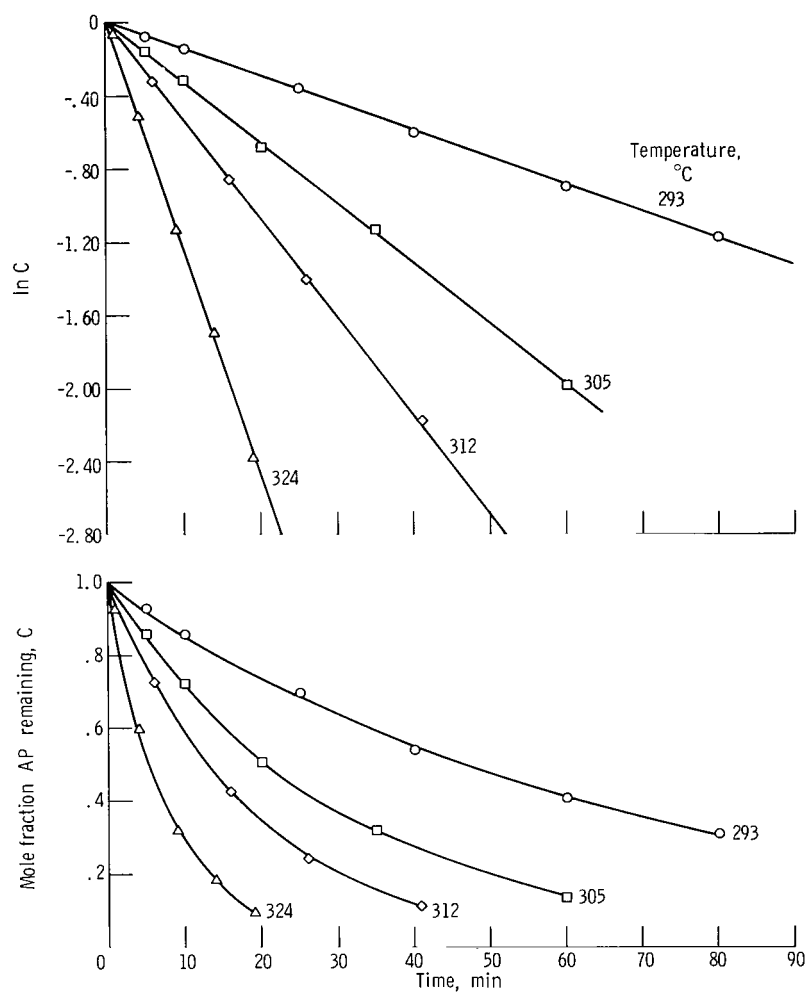


Figure 6. - Fraction of undecomposed ammonium perchlorate (AP) at 25 kilobars ($2.5 \times 10^9 \text{ N/m}^2$).

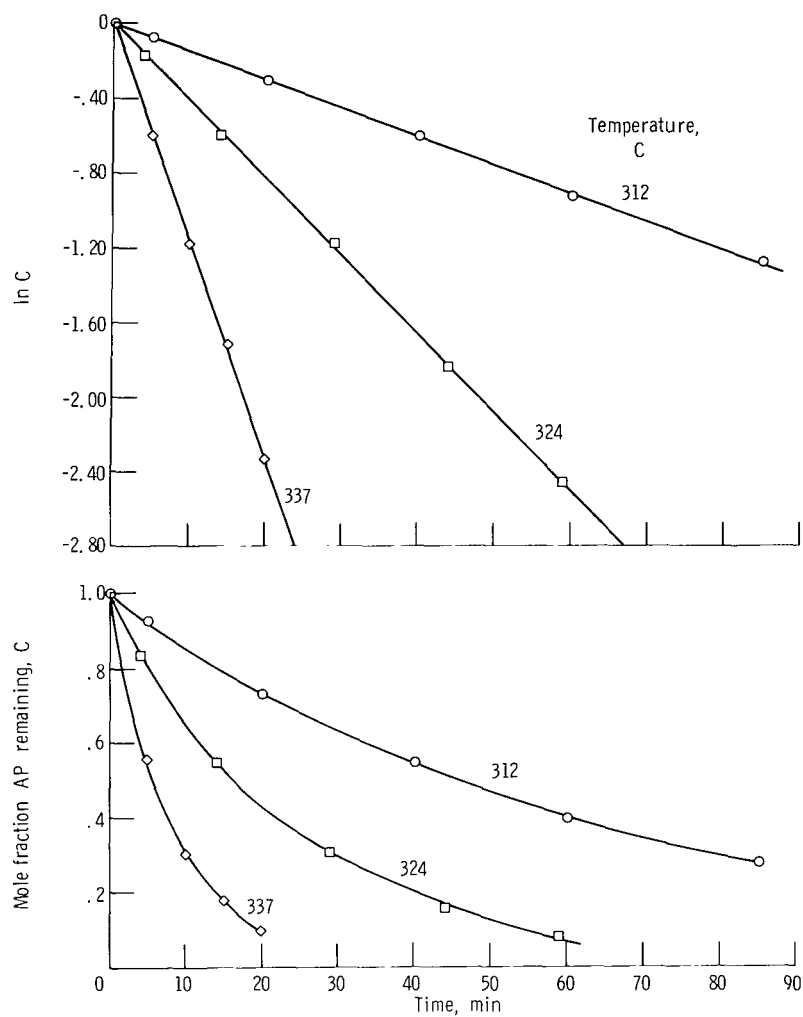


Figure 7. - Fraction of undecomposed ammonium perchlorate (AP) at 50 kilobars ($5.0 \times 10^9 \text{ N/m}^2$).

TABLE II. - SPECIFIC REACTION RATES FOR DECOMPOSITION

OF AMMONIUM PERCHLORATE

Pressure, kbar (N/m^2)					
15 (1.5×10^9)		25 (2.5×10^9)		50 (5.0×10^9)	
Temperature, $^{\circ}\text{C}$	Average reaction-rate constant, k , sec^{-1}	Temperature, $^{\circ}\text{C}$	Average reaction-rate constant, k , sec^{-1}	Temperature, $^{\circ}\text{C}$	Average reaction-rate constant, k , sec^{-1}
282	2.12×10^{-4}	293	2.46×10^{-4}	312	2.54×10^{-4}
295	4.53×10^{-4}	305	5.50×10^{-4}	324	7.01×10^{-4}
305	1.00×10^{-3}	312	8.80×10^{-4}	337	1.92×10^{-3}
316	1.77×10^{-3}	324	2.10×10^{-3}		

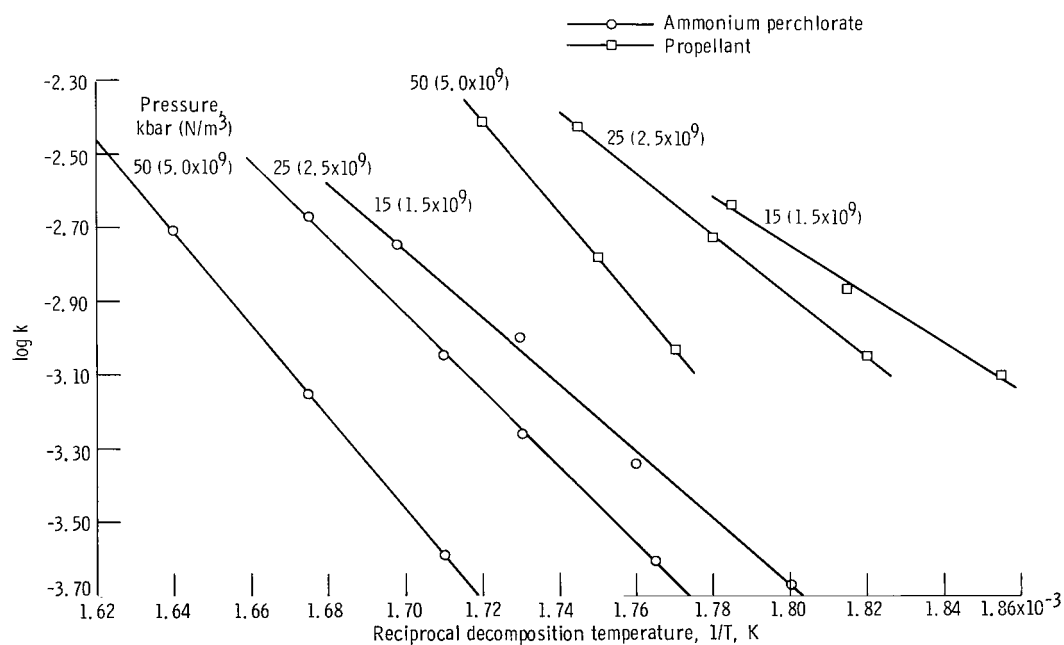


Figure 8. - Arrhenius plots of thermal decompositions at high pressures.

different temperatures and pressures which followed first-order kinetics. The data are represented by straight lines for the three pressures from which activation energies were calculated. The values found were 40.4 kilocalories per mole (1.69×10^5 J/mole) at 15 kilobars (1.5×10^9 N/m²), 46.3 kilocalories per mole (1.94×10^5 J/mole) at 25 kilobars (2.5×10^9 N/m²), and 57.2 kilocalories per mole (2.39×10^5 J/mole) at 50 kilobars (5.0×10^9 N/m²).

The rate equation for the thermal decomposition of AP at 15 kilobars (1.5×10^9 N/m²) was calculated to be

$$k = 2.05 \times 10^{12} e^{-40400/RT} \text{ sec}^{-1}$$

The rate equation at 25 kilobars (2.5×10^9 N/m²) was found to be

$$k = 2.19 \times 10^{14} e^{-46300/RT} \text{ sec}^{-1}$$

At 50 kilobars (5.0×10^9 N/m²) the rate equation was calculated to be

$$k = 7.42 \times 10^{17} e^{-57200/RT} \text{ sec}^{-1}$$

Preexplosion Kinetics (AP Propellant)

Kinetic data in the temperature range 266° to 308° C were obtained for the thermal decomposition of an AP solid propellant at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and 5.0×10^9 N/m²). Results similar to those for pure AP decomposition were obtained. Plots of the logarithm of the fraction of undecomposed propellant against time produced approximately straight lines. The data are tabulated in table III. Specific reaction-rate constants were calculated from the slopes of the aforementioned lines and are shown in table IV.

Arrhenius plots of log rate constants against $1/T$ at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and 5.0×10^9 N/m²) are shown in figure 8. Straight lines were obtained which allowed the calculation of activation energies of decomposition.

The rate equation for the thermal decomposition of the propellant at 15 kilobars (1.5×10^9 N/m²) was calculated to be

$$k = 1.70 \times 10^9 e^{-30300/RT} \text{ sec}^{-1}$$

At 25 kilobars (2.5×10^9 N/m²) the rate equation was found to be

$$k = 4.66 \times 10^{11} e^{-36900/RT} \text{ sec}^{-1}$$

TABLE III. - DATA FOR PRESSURE RUNS (PROPELLANT)

Pressure, kbar (N/m^2)								
15 (1.5×10^9)			25 (2.5×10^9)			50 (5.0×10^9)		
Temperature, $^{\circ}\text{C}$	Time, min	Mole fraction remaining	Temperature, $^{\circ}\text{C}$	Time, min	Mole fraction remaining	Temperature, $^{\circ}\text{C}$	Time, min	Mole fraction remaining
266	5.5	0.766	277	5	0.748	289	5	0.752
	15.5	.477		10	.589		10	.571
	30.5	.193		15	.449		15	.426
	45.5	.089		25	.256		20	.300
278	1	0.910	289	5	0.558		25	.233
	6	.615		10	.332	297	5	0.613
	11	.407		15	.189		10	.353
	16	.270		20	.106		15	.232
	23.5	.145					20	.123
287	1	0.860	301	3	0.497	308	2.5	0.550
	6	.447		5	.340		5	.287
	11	.205		7.5	.178		7.5	.133
	16	.080		10	.106		10	.081

TABLE IV. - SPECIFIC REACTION RATES FOR DECOMPOSITION OF PROPELLANT

Pressure, kbar (N/m^2)					
15 ($1.5 \times 10^9 \text{ N/m}^2$)		25 (2.5×10^9)		50 (5.0×10^9)	
Temperature, $^{\circ}\text{C}$	Average reaction- rate constant, k, sec^{-1}	Temperature, $^{\circ}\text{C}$	Average reaction- rate constant, k, sec^{-1}	Temperature, $^{\circ}\text{C}$	Average reaction- rate constant, k, sec^{-1}
266	7.96×10^{-4}	277	9.04×10^{-4}	289	9.24×10^{-4}
278	1.36×10^{-3}	289	1.87×10^{-3}	297	1.65×10^{-3}
287	2.31×10^{-3}	301	3.74×10^{-3}	308	3.85×10^{-3}

At 50 kilobars ($5.0 \times 10^9 \text{ N/m}^2$) the rate equation was calculated to be

$$k = 8.05 \times 10^{15} e^{-48\,500/RT} \text{ sec}^{-1}$$

Figure 8 shows that the effect of increasing pressure is to reduce the rate of thermal decomposition. For an increase in applied pressure it is necessary to use a higher temperature in order to obtain a decomposition rate comparable to one at a lower temperature. A decrease in reaction rate with increasing pressure may be expected on the basis of Le Chatelier's principle. Since the decomposition of AP yields gaseous products occupying a greater volume than the starting material, the application of external pressure would favor retention of reactant, that is, retard the decomposition.

Other workers (refs. 12 and 13) have studied the effect of high pressure on the thermal decomposition of explosives. Increasing pressure altered the rate of decomposition; in most cases a decrease in rate was observed. Bridgman (ref. 14) studied the effect of high mechanical stress up to 100 000 atmospheres on solid explosives. He found that a combination of high temperature with high stress was needed to produce an explosion. In this work, pressures up to 80 kilobars ($8.0 \times 10^9 \text{ N/m}^2$) failed to produce explosions or any decomposition in AP at room temperature.

The variation of activation energy for the decomposition of AP and AP propellant at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and $5.0 \times 10^9 \text{ N/m}^2$) is shown in figure 9. The energy barrier for decomposition increases with increasing pressure. Extrapolation of the AP curve back to atmospheric pressure gives an activation energy of 29 to 30 kilocalories per mole (1.21×10^5 to $1.255 \times 10^5 \text{ J/mole}$). This value is in very good agreement with the results obtained by Galwey and Jacobs (ref. 3) for the decomposition of AP pellets at 1 atmosphere (28 to 31 kcal/mole or 1.17 to 1.30 J/mole). Similar values were obtained by Bircumshaw and Newman (ref. 2). It should be pointed out that the activation energies calculated at atmospheric pressure were derived from different kinetic equations. Those workers used the Prout-Tompkins (ref. 15) and Avrami-Erofe'ev equations (refs. 16 and 17). The data for the decompositions of the present study were fitted to the Arrhenius equation. The data did not fit either the Prout-Tompkins or the Avrami-Erofe'ev equations.

Explosion Limits

Explosion limits for pure AP and AP containing aluminum powder and copper chromite up to 30 kilobars ($3.0 \times 10^9 \text{ N/m}^2$) pressure are shown in figure 10. The areas above the curves represent explosive regions. In all cases increasing pressure results in higher explosion temperatures. Addition of finely divided aluminum and copper chro-

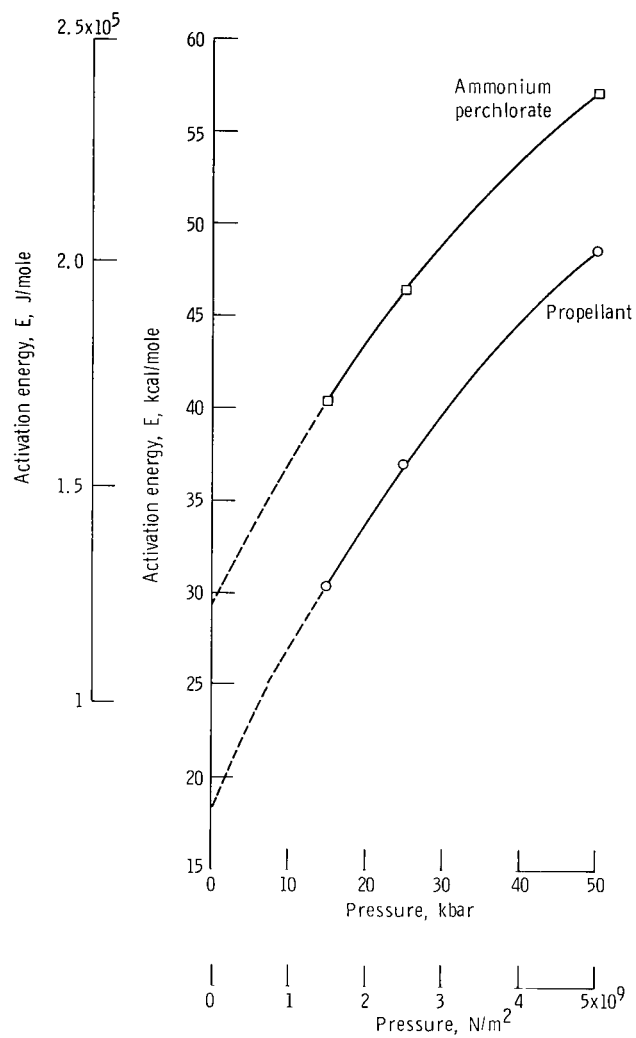


Figure 9. - Variation of activation energy of decomposition with pressure.

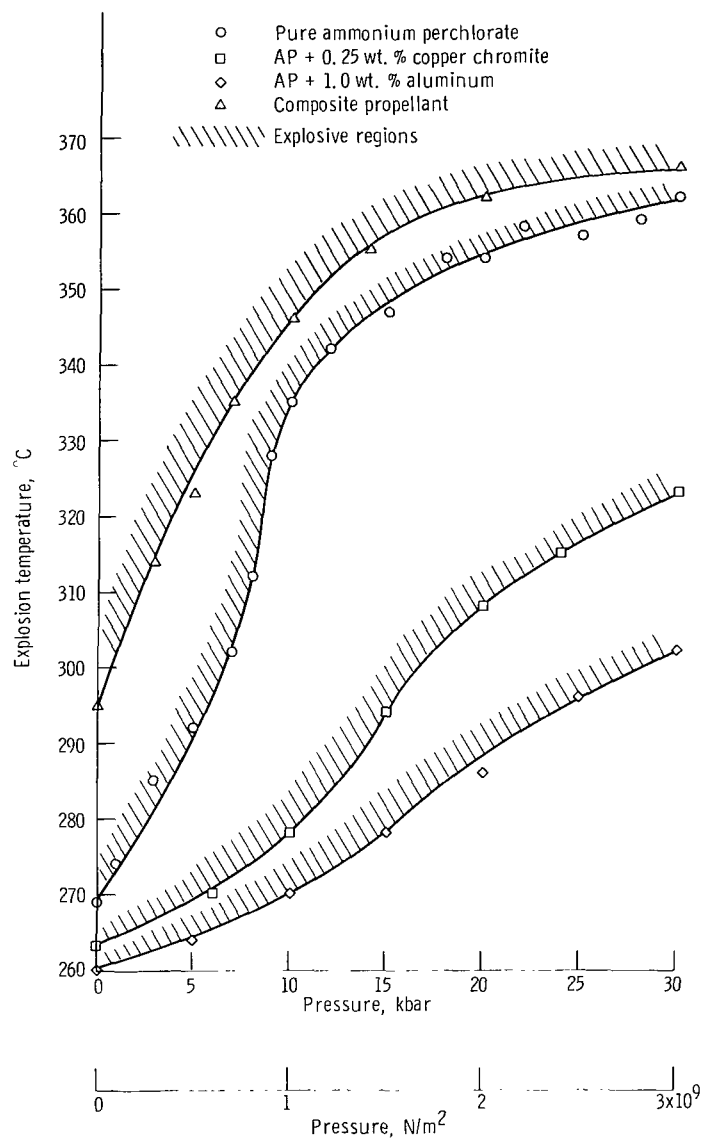


Figure 10. - Explosion limits of ammonium perchlorate (AP) and propellant at high pressure.

mite causes a considerable reduction in explosion temperature.

Since the decomposition of AP is an exothermic reaction, temperature is the main factor which distinguishes the conditions of explosion from those of slow decomposition. An explosion results when the rate of heat production by chemical decomposition exceeds the rate of heat loss to the surroundings.

It is clear from the results that the effect of pressure is to hinder the initiation of explosion. This fact could be predicted on the basis of Le Chatelier's principle. Since an explosion is a chemical reaction yielding products at high pressure, the external application of pressure should hinder explosion.

Since aluminum and copper chromite act as catalysts for the decomposition of ammonium perchlorate, it should be expected that lower initiation temperatures would be required. The reason for the higher explosion temperatures of the propellant as compared to pure AP may be due to the binder (80 percent by weight of the propellant) acting as an inhibitor.

Electrical Resistance

The temperature dependence of resistance of AP at high pressure is given in figure 11. Isobar I shows the resistance behavior for the first heating at 10 kilobars ($1.0 \times 10^9 \text{ N/m}^2$); isobar II represents the cooling curve. Additional temperature cycling

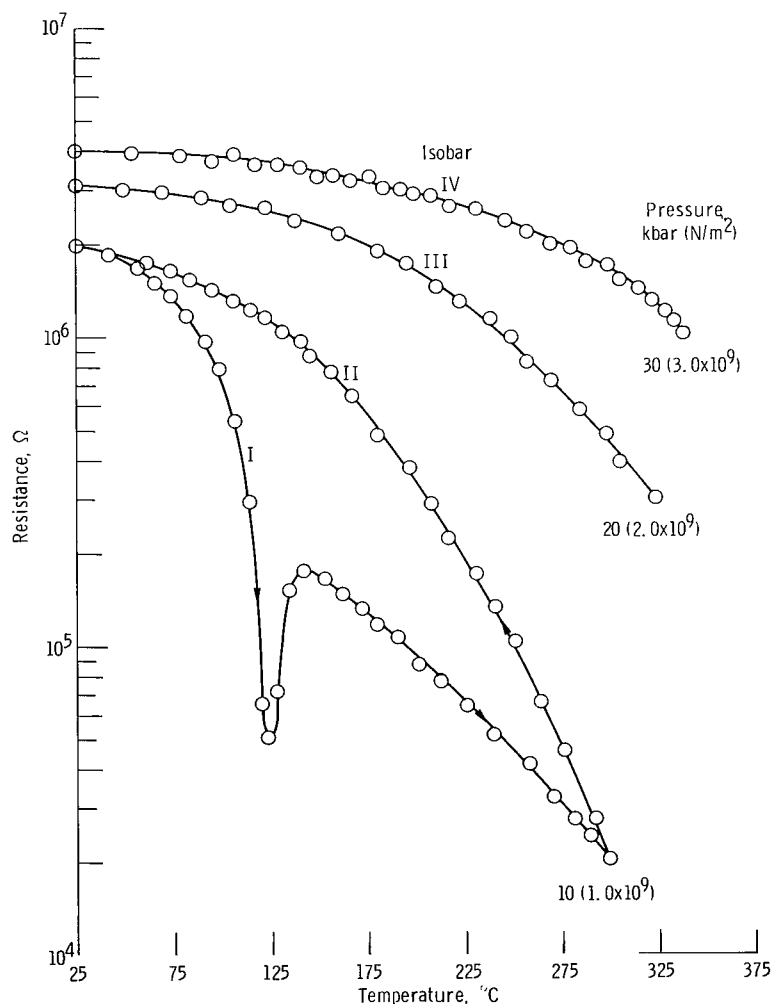


Figure 11. - Electrical resistance of ammonium perchlorate at high pressure.

at 10 kilobars ($1.0 \times 10^9 \text{ N/m}^2$) is also represented by isobar II. Isobars III and IV show resistance at 20 and 30 kilobars (2.0×10^9 and $3.0 \times 10^9 \text{ N/m}^2$), respectively.

The type of resistance minimum in isobar I at approximately 125°C is usually associated with a phase transformation. However, this probability was ruled out because the cooling curve and temperature cycling showed no minimum. Also, X-ray powder diagrams of recovered AP were identical with starting material. The density of AP samples prepared in the pellet mold was 1.92 grams per cubic centimeter. After compression to 10 kilobars ($1.0 \times 10^9 \text{ N/m}^2$) and heating to 300°C , the density increased to the single crystal value of 1.95 grams per cubic centimeter. Thus, the resistance minimum is attributed to voids in the sample which are removed during the first compression and heating.

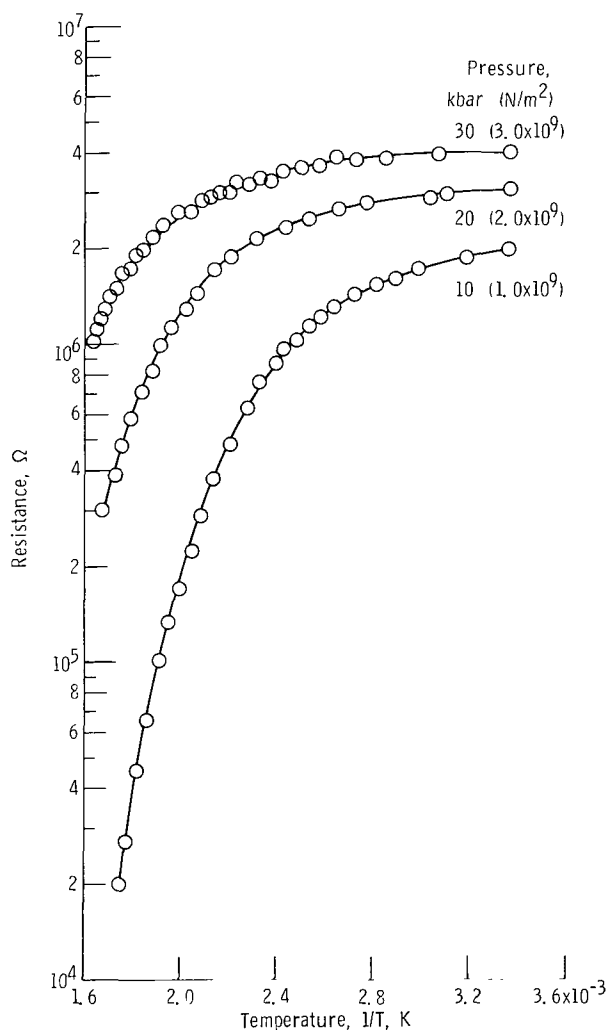


Figure 12. - Electrical resistance of ammonium perchlorate as function of temperature.

Tantalum foil was the best material for electrical contacts in resistance measurements. This material was found to be inert to AP under the high temperatures and pressures used in this study. Platinum and molybdenum were unsuitable for making resistance measurements. Under the aforementioned conditions these metals were attacked by AP and gave unreproducible resistance curves.

Ammonium perchlorate undergoes a phase transformation in the temperature range 240° to 270° C at atmospheric pressure (refs. 18 and 19). The crystal change is from the orthorhombic to the cubic form. Maycock, Verneker, and Gorzynski (ref. 20) studied the electrical conductivity of AP in the temperature range 60° to 280° C. Their plot of conductivity as a function of temperature showed a "knee" at 255° C which is attributed to the change in crystal structure. The plot of electrical resistance against reciprocal temperature at 10, 20, and 30 kilobars (1.0×10^9 , 2.0×10^9 , and 3.0×10^9 N/m²) in figure 12 shows none of the discontinuities usually associated with phase changes. It is possible the application of high pressure prevents the transformation, since there is a 9.7-percent increase in volume associated with the transition. The temperature shift of the transition as a function of pressure can be calculated by the Clapeyron-Clausius equation (ref. 21):

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_c - V_o)}$$

where ΔH is the enthalpy of transition, T is the absolute temperature, V_c is the molar volume of cubic AP, equal to 5.682×10^{-4} liter per gram ($0.5682 \text{ cm}^3/\text{g}$), and V_o is the molar volume of orthorhombic AP, equal to 5.128×10^{-4} liter per gram ($0.5128 \text{ cm}^3/\text{g}$). Using 2.3 kilocalories per mole (9.62×10^3 J/mole) for the enthalpy of transition (endothermic) as measured by Markowitz and Boryta (ref. 22) and the factor for converting calories to liter-atmospheres

$$\frac{0.08205 \text{ (liter-atm)(deg}^{-1}\text{)(mole}^{-1}\text{)}}{1.987 \text{ (cal)(deg}^{-1}\text{)(mole}^{-1}\text{)}} = 0.04129 \text{ (liter-atm)(cal}^{-1}\text{)}$$

or

$$\frac{82.05 \text{ (cm}^3\text{-atm)(deg}^{-1}\text{)(mole}^{-1}\text{)}}{8.314 \times 10^3 \text{ (J)(deg}^{-1}\text{)(mole}^{-1}\text{)}} = 9.8694 \text{ (cm}^3\text{-atm)(J}^{-1}\text{)}$$

one obtains

$$\frac{dp}{dT} = \frac{[2300 \text{ (cal)(mole}^{-1})][0.04129 \text{ (liter-atm)(cal}^{-1})]}{(513 \text{ deg})[5.54 \times 10^{-5} \text{ (liter)(g}^{-1})][117.5 \text{ (g)(mole}^{-1})]}$$

or

$$\begin{aligned} \frac{dp}{dT} &= \frac{[9.62 \times 10^6 \text{ (J)(mole}^{-1})][9.8694 \text{ (cm}^3\text{-atm)(J}^{-1})]}{(513 \text{ deg})[5.54 \times 10^{-2} \text{ (cm}^3\text{)(g}^{-1})][117.5 \text{ (g)(mole}^{-1})]} \\ &= 28.4 \text{ (atm)(deg}^{-1}) \end{aligned}$$

The reciprocal, $dT/dp = 0.035$ degree per atmosphere, indicates that an increase in pressure of 1 atmosphere raises the transition point 0.035 degree. A pressure of 10 kilobars ($1.0 \times 10^9 \text{ N/m}^2$) should raise the transition point approximately 350 degrees to about 590° C . This is obviously impossible, as shown by the explosion limit data at high pressure. High pressure X-ray measurements would be useful for determining the transition point of AP as a function of pressure. Such a method would clearly detect the orthorhombic to cubic transition.

SUMMARY OF RESULTS

The more significant results obtained from this study of solid ammonium perchlorate and an ammonium perchlorate based solid propellant at high pressures were as follows:

1. Thermal decompositions of AP and propellant at high pressure and elevated temperatures follow first-order kinetics and go to completion. Rate equations for the decomposition of perchlorate between 282° and 337° C at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and $5.0 \times 10^9 \text{ N/m}^2$) were calculated. Rate equations for decomposition of propellant between 266° and 308° C at 15, 25, and 50 kilobars (1.5×10^9 , 2.5×10^9 , and $5.0 \times 10^9 \text{ N/m}^2$) were calculated.
2. Explosion limits for ammonium perchlorate were determined to 30 kilobars ($3.0 \times 10^9 \text{ N/m}^2$). Increasing pressure raises explosion temperatures. Metallic additives lower explosion temperatures.
3. A composite propellant containing ammonium perchlorate has higher explosion temperatures than pure AP alone.

4. Electrical resistance measurements of compacted polycrystalline ammonium perchlorate powder suggested no phase transformations up to 30 kilobars (3.0×10^9 N/m²) and 340° C.

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